THERMODYNAMIC LENGTH IN A 2-D THERMODYNAMIC STATE SPACE

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ABSTRACT. The main goal of this paper is to reach an explicit formulation and possible interpretation of thermodynamic length in a thermodynamic state space with two degrees of freedom. Using the energy and entropy metric in a general form, we get explicit results about thermodynamic length along isotherms, its relation with work and with speed of sound. We also look at the relation between the determinants of the energy and entropy metrics and find that they differ by a factor of T^4.

1. INTRODUCTION

The concept of thermodynamic length defined by using either the energy or the entropy metric were introduced by F.Weinhold,[10] and G.Ruppeiner,[4] and later used by P. Salamon,[5−8], R.S. Berry,[5,7,8], J. Nulton,[6], E. Ihrig,[6] and others to study thermodynamic length. In particular, Salamon, Nulton and Ihrig [6] found that thermodynamic length using the entropy and energy metrics differs by a factor of the square root of mean temperature during a thermodynamic process and that, dimensionally, length is the square root of energy or it has the dimension of velocity if internal energy is given per unit mass.[7] It is also shown explicitly an expression for the length of an ideal gas at constant volume, pressure and entropy. We go a step further showing explicitly a possible interpretation of length in a general two dimensional thermodynamic state space with both metrics along isotherms. We find an expression for thermodynamic length in terms of extensive variables both in integral and differential form, its relation with the determinant of the metrics and the speed of sound. We also show the case when length is a measure of work done by the system and an interesting relation between the determinants of the two metrics.

2. Thermodynamic length with the energy metric

The thermodynamic length between two points a_0 and a_1 in thermodynamic state space is given by the following equation

$$L_{a_0 a_1} = \int_{a_0}^{a_1} [\sum_{i,j} \eta_{ij} dX_i dX_j]^{\frac{1}{2}} \tag{2.1}$$

where η_{ij} are elements of the thermodynamic metric and X_i represent independent coordinates in thermodynamic state space. We are going to study thermodynamic length with both the energy and entropy metric in a two dimensional state space with the purpose of relating length to the "degeneracy" of the thermodynamical state space and, for a restricted class of systems, to the concept of work.

This manuscript will unfold in a sequence of three main points. The first is that, as we shall see, thermodynamic length of a thermodynamical system with two degrees of freedom goes to zero as the system reaches its critical point and, therefore, as curvature blows up. The second is that also the speed of sound goes to zero close to criticality and the third is that for Ideal and "quasi-Ideal" thermodynamical systems,(see Remark 1 below), thermodynamic length is proportional to work as long as we keep the temperature of the (reversible) process constant. In particular, it would be reasonable to think that length could quantify the amount of work done by a "quasi-Ideal" system to keep its equilibrium.

We first consider the energy representation in which the molar internal energy is given by $u = u(s, v)$ where s, the molar entropy, and v, the molar volume, are the two independent variables.

Then the metric for such a system is given by,[3]

$$\eta_{ij_u} = \frac{1}{c_v} \begin{pmatrix} T & -\frac{T\alpha}{k_T} \\ -\frac{T\alpha}{k_T} & \frac{c_p}{v k_T} \end{pmatrix} \tag{2.2}$$

where

(1) c_v is the molar heat capacity at constant volume:

$$c_v = T(\frac{\partial s}{\partial T})_v \qquad , \tag{2.3}$$

(2) c_p is the molar heat capacity at constant pressure:

$$c_p = T(\frac{\partial s}{\partial T})_p \qquad , \qquad (2.4)$$

(3) α is the thermal coefficient of expansion:

$$\alpha = \frac{1}{v}(\frac{\partial v}{\partial T})_p \qquad , \qquad (2.5)$$

(4) κ_T is the isothermal compressibility:

$$\kappa_T = -\frac{1}{v}(\frac{\partial v}{\partial p})_T \qquad . \qquad (2.6)$$

Therefore the thermodynamic length in the energy metric with entropy and volume becomes

$$L = \int [\frac{T}{c_v}(ds)^2 - 2\frac{T\alpha}{\kappa_T c_v}dsdv + \frac{c_p}{v\kappa_T c_v}(dv)^2]^{\frac{1}{2}}$$

$$= \int \sqrt{\frac{T}{c_v}[ds - \frac{\alpha}{\kappa_T}dv]^2 + \frac{1}{v\kappa_T}(dv)^2} \qquad (2.7)$$

In general, molar entropy and volume could be given parametrically as $s = s(\xi)$, $v = v(\xi)$. Then the thermodynamic length would be given by,[7]

$$L = \int_{\xi_i}^{\xi_f} [\frac{T}{c_v}(\frac{ds}{d\xi})^2 - 2\frac{T\alpha}{\kappa_T c_v}\frac{ds}{d\xi}\frac{dv}{d\xi} + \frac{c_p}{v\kappa_T c_v}(\frac{dv}{d\xi})^2]^{\frac{1}{2}}d\xi \qquad (2.8)$$

Generalizing the work done by Salamon, Andresen, Gait and Berry[7], the length for a reversible process at constant molar entropy reduces to

$$L^s = \int \sqrt{\frac{c_p}{c_v v\kappa_T}}dv = \int \sqrt{\eta_{22}}dv \qquad . \qquad (2.9)$$

but, since $\det (\eta_{ij})_u = \frac{T}{\kappa_T v c_v} = -\frac{T}{c_v}(\frac{\partial p}{\partial v})_T$, then $\kappa_T = \frac{T}{vc_v \det (\eta_{ij})_u}$ and we have

$$L^s = \int \sqrt{\frac{c_p}{T}\det(\eta_{ij})_u}dv \qquad (2.10)$$

We can also look at the integration (2.7) with respect to molar volume being constant. In this case we get,

$$L^v = \int \sqrt{\frac{T}{c_v}}ds = \int \sqrt{\eta_{11}}ds \qquad (2.11)$$

Like (2.10), we also have

$$L^v = \int \sqrt{v \kappa_T \det(\eta_{ij})_u} ds \tag{2.12}$$

It is reasonable to think that the determinant of the matrix would be a "measure" of how close a system is to the critical point. Indeed, if $\det(\eta_{ij})_u = 0$ then we have a curve of degeneracy along which curvature blows up and , therefore, thermodynamical phase space become extremely curved. So, whenever this event happens, length approaches zero and, as below is shown, the speed of sound goes to zero.

We could also look at length at constant pressure. Then we get

$$L^p = \int \sqrt{\frac{c_p}{T v^2 \alpha^2}} dv \tag{2.13}$$

Let's look, now, at the relation between length and speed of sound. Let's denote with ν^i_{sound} and ν^a_{sound} respectively the speed of sound in terms of isothermal and adiabatic compressibility κ_T and κ_S. We can, now, look at the relation between speed of sound and the determinant of the matrix(and therefore curvature) being aware of the fact that κ_S is used the most. So, since $\nu^i_{sound} = \sqrt{\frac{1}{\kappa_T \rho}}$, we have the following

$$\nu^i_{sound} = \sqrt{\frac{v c_v \det(\eta_{ij})_u}{T \rho}} \tag{2.14}$$

and, since $\nu^a_{sound} = \sqrt{\frac{1}{\kappa_S \rho}}$, with $\kappa_S = \frac{c_v}{c_p} \kappa_T$, then

$$\nu^a_{sound} = \sqrt{\frac{v c_p \det(\eta_{ij})_u}{T \rho}} \tag{2.15}$$

with ρ being the density of the gas. It easily follows then

$$\nu^i_{sound} = \left(\sqrt{\frac{c_p}{c_v}}\right) \nu^a_{sound} \tag{2.16}$$

We can write the thermodynamic length in terms of speed of sound, namely,

$$L = \int \nu^i_{sound}\sqrt{\frac{c_p\rho}{c_v v}}dv = \int \nu^a_{sound}\sqrt{\frac{\rho}{v}}dv = \int \nu^i_{sound}\sqrt{\frac{T\kappa_T\rho}{c_v}}ds = \int \nu^a_{sound}\sqrt{\frac{T\kappa_T\rho}{c_p}}ds \tag{2.17}$$

Therefore, we get

$$\frac{dL}{dv} = \nu^i_{sound}\sqrt{\frac{c_p\rho}{c_v v}} = \nu^a_{sound}\sqrt{\frac{\rho}{v}} \tag{2.18}$$

and

$$\frac{dL}{ds} = \nu^i_{sound}\sqrt{\frac{T\kappa_T\rho}{c_v}} = \nu^a_{sound}\sqrt{\frac{T\kappa_T\rho}{c_p}} \tag{2.19}$$

It is evident that

$$\frac{dL}{dv} \geq 0 \qquad \frac{dL}{ds} \geq 0$$

Moreover, since $\frac{c_p}{c_v v \kappa_T} = (\frac{\partial^2 u}{\partial v^2})_s = \eta_{22}$ and $\frac{T}{c_v} = (\frac{\partial^2 u}{\partial s^2})_v = \eta_{11}$, then (2.9) and (2.11) tell us that

$$(\frac{dL}{dv})^2 = (\frac{\partial^2 u}{\partial v^2})_s = \eta_{22} \tag{2.20}$$

and

$$(\frac{dL}{ds})^2 = (\frac{\partial^2 u}{\partial s^2})_v = \eta_{11} \tag{2.21}$$

Proposition 1. *The molar internal energy of the system has the form $u = a(s)v+b(s)$ if and only if the thermodynamic length L is independent on volume density;(v is the isotropic direction).*

Proposition 2. *The molar internal energy of the system has the form $u = c(v)s+d(v)$ if and only if the thermodynamic length L is independent on molar entropy; (s is the isotropic direction).*

Proof. Immediate from (2.20) and (2.21)■.

It is interesting to look now at the relation between thermodynamic length and work and we'll try to give a possible interpretation of what length would mean in a thermodynamical system along isotherms . It is shown, indeed, by the following theorem and remark that if our system is ideal or "quasi-ideal" then thermodynamic length is work just along isotherms.

Theorem 1. *Let's consider the Ideal gas whose pressure is given by*

$$|(\frac{\partial u}{\partial v})_s| = |p| = \frac{RT}{v} \tag{2.22}$$

then, along isotherms,

$$L^s = \frac{1}{\sqrt{RT}}W \tag{2.23}$$

where W is work.

Proof.
Consider the case in which

$$(\frac{\partial^2 u}{\partial v^2})_s = \frac{1}{RT}[(\frac{\partial u}{\partial v})_s]^2 \tag{2.24}$$

where u is the molar internal energy. Naturally, (2.24) is equivalent to

$$(\frac{\partial p}{\partial v})_s + \frac{1}{RT}p^2 = 0 \tag{2.25}$$

since $(\frac{\partial^2 u}{\partial v^2})_s = -(\frac{\partial p}{\partial v})_s$ and $(\frac{\partial u}{\partial v})_s = -p$. Now, (2.25) is a separable first order differential equation whose solution is given by

$$p = \frac{RT}{v}$$

As solution of (2.24) we have $u = -RT \ln|v|$. Then, by (2.9)

$$L^s = \int \sqrt{(\frac{\partial^2 u}{\partial v^2})_s}dv = \int \sqrt{\frac{1}{RT}(\frac{\partial u}{\partial v})_s^2}dv = \int \sqrt{\frac{1}{RT}}|(\frac{\partial u}{\partial v})_s|dv = \sqrt{\frac{1}{RT}}\int |p|dv = \sqrt{\frac{1}{RT}}W■$$
$$\tag{2.26}$$

Remark 1. Note that the statement of Theorem 1 is true also for a more general case in which we consider the volume occupied by molecules inside the system. Namely the "quasi-Ideal" case in which pressure is expressed in the form $p = \frac{RT}{v-b}$.

Remark 2. It is also extremely important to note that, while $\eta_{22} = \frac{c_p p}{c_v v}$ for a general two dimensional Ideal Gas, it becomes $\eta_{22} = \frac{RT}{v^2}$ along isotherms.

So, this theorem gives us a first understanding of the relation between thermodynamic length and work in explicit form along and just along isotherms.

Corollary 1. *Thermodynamic length measures the amount of work done by a "quasi-ideal" system along isotherms.*

By quasi-ideal we mean that b might as well be different than zero. Therefore the system is not completely ideal.

Remark 3. It is interesting to note that equation (2.24) is of the form $u_{vv} = \frac{1}{RT}(u_v)^2$ with u parametrized by molar volume. As the volume decreases, the system applies a resistance in the opposite (positive) direction by $\frac{1}{RT}$ (constant). The length, then, would probably measure the amount of work done by the system to keep its equilibrium state, always along isotherms.

3. Thermodynamic length with the entropy metric

Let's now discuss what happens when we look at the entropy metric. Consider $s = s(u, v)$ where u is the energy of the system per unit mole. In this case molar internal energy and molar volume are the independent variables. If we let $\eta_{ij_s} = -\frac{\partial^2 s(X)}{\partial X_i \partial X_j}$, then the metric is given by,(see also the paper by Mrugala[3]),

$$\eta_{ij_s} = \frac{1}{c_v T^2} \begin{pmatrix} 1 & -(\frac{T\alpha - \kappa_T p}{\kappa_T}) \\ -(\frac{T\alpha - \kappa_T p}{\kappa_T}) & (\frac{T\alpha - \kappa_T p}{\kappa_T})^2 + \frac{c_v T}{v \kappa_T} \end{pmatrix} \tag{3.1}$$

Then the thermodynamical length is given by

$$L = \int [\frac{1}{c_v T^2}(du)^2 - \frac{2}{T^2}(\frac{T\alpha - \kappa_T p}{\kappa_T c_v})dudv + [\frac{1}{c_v}(\frac{T\alpha - \kappa_T p}{T \kappa_T})^2 + \frac{1}{v \kappa_T T}(dv)^2]]^{\frac{1}{2}}$$

$$= \int [\frac{1}{c_v T^2}[du - (\frac{T\alpha - \kappa_T p}{\kappa_T})dv]^2 + \frac{1}{v\kappa_T T}(dv)^2]^{\frac{1}{2}} \qquad (3.2)$$

Then, thermodynamic length at constant molar internal energy and constant molar volume is given by

$$L^u = \int \sqrt{\frac{1}{c_v T^2}(\frac{T\alpha - \kappa_T p}{T\kappa_T})^2 + \frac{1}{v\kappa_T T}} dv = \int \sqrt{\eta_{22}} dv \qquad (3.3)$$

and

$$L^v = \int \sqrt{\frac{1}{c_v T^2}} du = \int \sqrt{\eta_{11}} du \qquad (3.4)$$

Expressing the thermodynamic length in terms of the determinant of the entropy metric which is given by $\det(\eta_{ij})_s = \frac{1}{vT^3 c_v \kappa_T} = -\frac{1}{c_v T^3}(\frac{\partial p}{\partial v})_T$, we get

$$L^u = \int \sqrt{[\frac{v}{\kappa_T T}(T\alpha - p\kappa_T)^2 + T^2 c_v] \det(\eta_{ij})_s} dv \qquad (3.5)$$

and

$$L^v = \int \sqrt{Tv\kappa_T \det(\eta_{ij})_s} du \qquad (3.6)$$

Moreover, we can consider the speed of sound both isothermal and adiabatic with respect to the entropy metric

$$\nu^i_{sound} = \sqrt{\frac{vc_v T^3 \det(\eta_{ij})_s}{\rho}} \qquad (3.7)$$

and

$$\nu^a_{sound} = \sqrt{\frac{vc_p T^3 \det(\eta_{ij})_s}{\rho}} \qquad (3.8)$$

and write the thermodynamic length in terms of speed of sound

$$L = \int \nu^i_{sound} \sqrt{\frac{\rho}{Tv}[1 + \frac{v}{T^3 c_v \kappa_T}(T\alpha - p\kappa_T)^2]} dv = \int \nu^i_{sound} \sqrt{\frac{\rho\kappa_T}{T^2 c_v}} du \qquad (3.9)$$

Naturally $\frac{dL}{dv} \geq 0$ and $\frac{dL}{du} \geq 0$.

As for the energy metric,(see (2.20) and (2.21)), we have the following propositions:

Proposition 3. *The molar entropy of the system has the form $s = a(u)v + b(u)$ if and only if the thermodynamic length L is independent on volume density; (v is the isotropic direction).*

Proposition 4. *The molar entropy of the system has the form $s = c(v)u + b(v)$ if and only if the thermodynamic length L is independent on molar internal energy; (u is the isotropic direction).*

Also with the entropy metric we come to the conclusion that thermodynamic length is somehow related to work just along isotherms in case of Ideal and quasi-Ideal Gas. The following theorem shows the Ideal case while the quasi-ideal is trivial as in the case of the energy metric.

Theorem 2. *Let's consider the Ideal Gas with*

$$|(\frac{\partial s}{\partial v})_u| = |(\frac{p}{T})| = \frac{R}{v} \tag{3.10}$$

then, along isotherms,

$$L^u = \sqrt{\frac{1}{RT^2}}W \tag{3.11}$$

where W is work.

Proof.

The following separable first order differential equation $(\frac{\partial(p/T)}{\partial v})_u + \frac{1}{R}(\frac{p}{T})^2 = 0$ which is equivalent to

$$(\frac{\partial^2 s}{\partial v^2})_u = -\frac{1}{R}[(\frac{\partial s}{\partial v})_u]^2 \tag{3.12}$$

has solution $p = \frac{RT}{v}$.

Therefore (3.3) becomes

$$L^u = \int \sqrt{(\frac{\partial^2 s}{\partial v^2})_u}dv = \int \sqrt{\frac{1}{R}(\frac{\partial s}{\partial v})_u^2}dv = \int \sqrt{\frac{1}{R}}|(\frac{\partial s}{\partial v})_u|dv = \sqrt{\frac{1}{R}}\int |\frac{p}{T}|dv = \sqrt{\frac{1}{RT^2}}W \blacksquare$$

$$\tag{3.13}$$

Remark 4. Note that also in this case, the statement of Theorem 2 is true for a more general case in which the volume occupied by molecules inside the system is considered. Namely the "quasi-Ideal" case.

4. RELATION BETWEEN $\det(\eta_{ij})_u$ AND $\det(\eta_{ij})_s$

We have found that the determinants of the two matrices (2.2) and (3.1) were given by

$$\det (\eta_{ij})_u = \frac{T}{\kappa_T v c_v} = -\frac{T}{c_v}(\frac{\partial p}{\partial v})_T \tag{4.1}$$

and

$$\det (\eta_{ij})_s = \frac{1}{v T^3 c_v \kappa_T} = -\frac{1}{c_v T^3}(\frac{\partial p}{\partial v})_T \tag{4.2}$$

Note that in case the entropy metric is considered to be the positive second partial derivative of entropy density with respect to the extensive variables than the signs of such expressions change. Now, comparing the two determinants we get the interesting result

$$\det(\eta_{ij})_u = T^4 \det(\eta_{ij})_s \tag{4.3}$$

It is important to emphasize relation (4.23) because of the factor T^4 which takes us to a possible connection with the Stefan-Boltzmann Law.

5. CONCLUSIONS

With this paper we have tried to make a possible connection between thermodynamic length and work using both energy and entropy metric. The possible interpretation that we have found is that for Ideal and quasi-Ideal gas, thermodynamic length "measures" the amount of work, along isotherms, that a thermodynamic system does to keep its ideal state or its equilibrium.

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